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Unsaturated oligophenol cyanates

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## Unsaturated oligophenol cyanates

The Invention relates to oligophenol cyanates of the general formula

$$[A-]_n[B-A-]_xB[-A]_m$$
 (I).

In this formula, A is in each case a group of the formula

and B is in each case a group of the formula

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 $R^1$ ,  $R^2$  and  $R^3$  on each group A independently of the others are in each case hydrogen or a bond to a group B with the proviso that each group A has either one or two bonds to B.

Both  $R^4$  and  $R^4$ , and  $R^5$  and  $R^5$ , on each group B independently of the others, are in each case either together a direct bond or, in any desired order, are hydrogen and a bond to a group A with the proviso that each group B has either one or two bonds to A.

The indices m and n are 0 or 1 and x is an integer from 0 to 10 with the proviso that at least one of the numbers m, n and x is other than 0 and m and n are not both at the same time 1.

The Invention also relates in particular to mixtures of such compounds with one another and/or with those compounds of the

formula I in which m and n deviate from the above definitions by both being 1.

Saturated oligophenol cyanates of general formula I in which m and n deviate from the compounds of the present invention by both being 1 are known, for example, from EP-A-0 147 548 and are marketed by the Dow Chemical Co. under the designation XU71787. These compounds do not have any olefinic double bonds and are therefore able to polymerize only by cyclotrimerization of the cyanate groups or by reaction with functional groups of other compounds. The cyclotrimerization requires the presence of catalysts and/or high temperatures. In contrast it is often desirable to achieve partial curing or crosslinking by means, for example, of irradiation at room temperature. In addition, these known compounds have a relatively high viscosity, which is unfavourable for some applications.

The object of the present invention was therefore to provide oligophenol cyanates which have a low viscosity and which without further additives can be (partially) polymerized or crosslinked at room temperature by means, for example of radiation-induced free-radical reactions.

In accordance with the invention this object is achieved by the unsaturated eligophenol cyanates of the formula I in accordance with Claim 1. The molecule of these compounds has at least one olefinic double bond  $(R^4-R^4')$  and/or  $R^5-R^5'$  according to formula I) which permits free-radical addition polymerization.

The olefinic double bonds are present in groups of the formula

30 The degree of polymerization, x, lies preferably between 0 and 5 and, with particular preference, between 0 and 3.

The unsaturated oligophenol cyanates of the invention can be prepared by reacting an oligophenol of the general formula

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Subs

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$$[A'-]_n[B-A'-]_xB[-A']_m$$
 (II),

in which A' is a group of the formula

$$R^3$$
 $R^2$ 
 $R^3$ 

and B,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^4$ ,  $R^5$ ,  $R^5$ ,  $R^5$ ,  $R^5$ , and  $R^4$  are as defined in Claim 1, is reacted with cyanogen chloride in the presence of a tertiary amine. Oligophenols\of formula II are obtainable from Borden Chemical Inc. under the designations ESD-X1 to -X5, ESD-473C. ESD-472C and The \compounds concerned condensation products of dicyclopentadiene (dimeric pentadiene) and phenol, which are present as a mixture of isomeric and/or homologous compounds and also contain fractions of saturated compounds where  $m = n = \lambda$ .

The preparation of the oligophenol cyanates of the invention is preferably carried out at a temperature of less than 10 °C in a polar solvent such as butyl acetate and/or acetone or methyl ethyl ketone, for example, or in mixtures of these solvents. Particularly preferred reaction temperatures are below 0 °C - for example, -10 °C. It is advantageous to employ 1.0-1.1 mol of tertiary amine and 1.0-1.2 mol of cyanogen chloride per OH equivalent of the oligophenol II. A particularly preferred tertiary amine is triethylamine.

The unsaturated oligophenol cyanates of the invention have a low viscosity at processing temperature and produce polytriazine resins having a particularly low dielectric constant. They are particularly suitable, for example, as matrix material for the production of fibre-reinforced composites, especially for

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components in aerospace technology, or as base materials for the of printed circuit boards. Owing to their viscosity and capacity for polymerization by means of high-energy radiation (UV, X-rays, y-rays or electron beams), they are also suitable for (photo)lithographic varnishes, solder resists for circuit boards, or other radiation-curable lacquers and coatings.

The following example illustrates the preparation of the oligophenol cyanates of the invention without constituting any restriction.

## Example

ESD-X3 (Borden Chemical Inc.) was dissolved Oligophenol n-butyl acetate/acetone (v/v = 80:20) to give a 15% strength cooled to -10  $^{\circ}$ C and, The solution was solution. temperature, 105% of the calculated amount of triethylamine and then, over the course of 30 minutes, 110% of the calculated amount of cyanogen chloride were added. After a further 30 minutes of reaction, the mixture was subjected to extraction with water, twice at 30 °C, in order to remove the ammonium salts formed, and was then passed twice through a falling-film evaporator in order to remove the solvent and the by-product, N, N-diethylcyanamide.

Yield: about 100%

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viscosity: 165 mPa·s (at 125°C)

degree of reaction: (phenol → cyanate) >98%

gel time: 25 min (at 200°C)

carbamates: <1%

30 N, N-diethylcyanamide: <2000 ppm